

# Adsorption and diffusion of H<sub>2</sub>O molecule on the Be(0001) surface: A density-functional theory study

Shuang-Xi Wang,<sup>1,2,3</sup> Peng Zhang,<sup>4</sup> Jian Zhao,<sup>5</sup> Shu-Shen Li,<sup>1</sup> and Ping Zhang<sup>3,\*</sup>

<sup>1</sup>*State Key Laboratory for Superlattices and Microstructures,  
Institute of Semiconductors, Chinese Academy of Sciences,  
P. O. Box 912, Beijing 100083, People's Republic of China*

<sup>2</sup>*Tsinghua, People's Republic of China*

<sup>3</sup>*LCP, Institute of Applied Physics and Computational Mathematics,  
P.O. Box 8009, Beijing 100088, People's Republic of China*

<sup>4</sup>*Department of Nuclear Science and Technology,  
Xi'an Jiaotong University, Xi'an 710049, People's Republic of China*

<sup>5</sup>*State Key Laboratory for Geomechanics and deep underground engineering,  
China University of Mining and Technology,  
Beijing 100083, People's Republic of China*

## Abstract

Using first-principles calculations, we systematically study the adsorption behavior of a single molecular H<sub>2</sub>O on the Be(0001) surface. We find that the favored molecular adsorption site is the top site with an adsorption energy of about 0.3 eV, together with the detailed electronic structure analysis, suggesting a weak binding strength of the H<sub>2</sub>O/Be(0001) surface. The adsorption interaction is mainly contributed by the overlapping between the *s* and *p<sub>z</sub>* states of the top-layer Be atom and the molecular orbitals 1*b*<sub>1</sub> and 3*a*<sub>1</sub> of H<sub>2</sub>O. The activation energy for H<sub>2</sub>O diffusion on the surface is about 0.3 eV. Meanwhile, our study indicates that no dissociation state exists for the H<sub>2</sub>O/Be(0001) surface.

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\*Corresponding author. zhang\_ping@iapcm.ac.cn

Water adsorption on metal surfaces has gained a lot of interest in a variety of phenomena such as heterogeneous catalysis and corrosion of materials [1, 2]. As a result these systems have been intensively investigated by various experimental and theoretical techniques. With respect to the substrates, most of the recent studies have focused on the transition metal surfaces, such as Cu(100) [3, 4], Fe(100) [5, 6], and Pd(100) [7, 8]. Although ambiguities exist, by early density-functional theory (DFT) calculations, theoretically a flat-lying configuration on the top site of transition metal surfaces has been established by some sophisticated studies [9–11], arguing that the molecular orbitals (MOs) of water, mainly  $1b_1$ , dominate the water-surface interaction, by coupling with atomic  $d$  orbital of the transition metal surfaces. In comparison with the vast studies on the adsorption properties of  $H_2O$  on transition metal surfaces, however, for simple metals which are lack of  $d$  states, very few researches [12] have been reported up to now. This long-term overlook should be altered by considering the fact that there is now an increasing practical demand for a thorough understanding of the water structures on some specific simple metals.

Motivated by this observation, in the present paper we use first-principles calculations to investigate the adsorption properties of  $H_2O$  on the Be(0001) surface. The reason why we choose beryllium as the prototype for simple metals is as follows: (i) beryllium has vast technological applications due to its high melting point and low weight. One of its important usage is as a plasma facing material in experimental nuclear fusion reactors [13]. As the first wall, the beryllium can adsorb the residual gases in the plasma vessel, improving the vacuum cleanliness [14]. Water is the main residual gas in the ultrahigh vacuum (UHV) vessels of the fusion reactors, so it is highly meaningful to study the adsorption of water molecule at beryllium surfaces; (ii) besides and prominently, different from the bulk, beryllium surfaces have a large directional  $s$  and  $p$  electronic distributions around the Fermi energy and thus may display unique interaction with the adsorbed  $H_2O$  molecules.

Through analysis of projected density of states (PDOS) and charge density difference, we obtain the adsorption properties of  $H_2O$  on the Be(0001) surface. It is found that the  $H_2O$  molecule prefers to adsorb on the surface top site in a fairly flat-lying configuration with a weak binding strength. The adsorption interaction is mainly characterized by the overlapping between the  $s$  and  $p_z$  states of the top-layer Be atom and the MOs  $1b_1$  and  $3a_1$  of the water molecule. We notice that different from transition metal surfaces, the MO  $3a_1$  plays an important role in the interaction between  $H_2O$  and Be(0001). The diffusion

energetics of H<sub>2</sub>O across the Be(0001) surface is also studied, which gives an activation barrier of  $\sim 0.3$  eV.

Our calculations are performed within DFT using the Vienna *ab-initio* simulation package (VASP) [16]. The PW91 [15] generalized gradient approximation and the projector-augmented wave potential [17] are employed to describe the exchange-correlation energy and the electron-ion interaction, respectively. The cutoff energy for the plane wave expansion is set to 400 eV. The Be(0001) surface is modeled by a slab composing of five atomic layers and a vacuum region of 20 Å. A  $3 \times 3$  supercell, in which each monolayer contains nine Be atoms, is adopted in the study of the H<sub>2</sub>O adsorption. The water is placed on one side of the slab only and a dipole correction [18] is applied to compensate for the induced dipole moment. During our calculations, the bottom two atomic layers of the Be surface are fixed, and other Be atoms as well as the H<sub>2</sub>O molecule are free to relax until the forces on the ions are less than 0.02 eV/Å. Integration over the Brillouin zone is done using the Monkhorst-Pack scheme [19] with  $7 \times 7 \times 1$  grid points. And a Fermi broadening [20] of 0.1 eV is chosen to smear the occupation of the bands around the Fermi energy ( $E_F$ ) by a finite- $T$  Fermi function and extrapolating to  $T = 0$  K.

The calculation of the energy barriers for the water diffusion processes is performed using the nudged elastic band (NEB) method [21], which is a method for calculating the minimum energy path between two known minimum energy sites, by introducing a number of “images” along the diffusion path. Then the energy barrier is determined by relaxing the atomic positions of each image in the direction perpendicular to the path connecting the images, until the force converges. In present work, the diffusion path is modeled using seven images, two of which include the minimum energy sites as initial and final positions, with five linearly interpolated, intermediate images between them.

The structural and energetic parameters of the free water molecule are calculated within a box with the same size of the adsorbed systems. The optimized geometry for free H<sub>2</sub>O gives a bond length of 0.97 Å and a bond angle of 104.4°, consistent with the experimental values of 0.96 Å and 104.4° [22]. The calculated lattice constant of bulk Be ( $a$ ,  $c$ ) are 2.26 Å and 3.58 Å, respectively, in good agreement with the experimental measurements of 2.29 Å and 3.588 Å [23].

As depicted in Fig. 1(a), there are four high-symmetry sites on the Be(0001) surface, respectively the top, bridge (bri), hcp and fcc hollow sites. H<sub>2</sub>O adsorption at all four

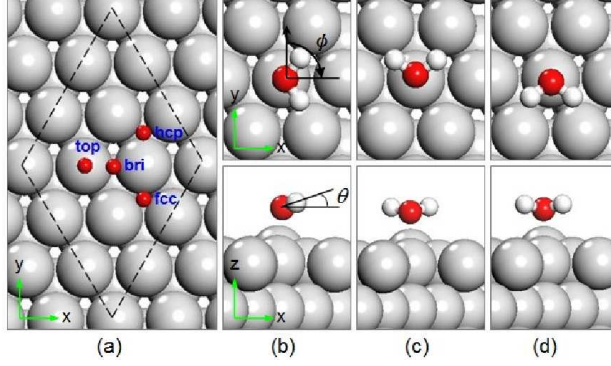


FIG. 1: (Color online) (a) The structure of the  $p(3 \times 3)$  surface cell of Be (0001), and three on-surface adsorption sites. The red balls denote the initial positions of O atoms in the adsorption picture. (b)-(d) Top view (upper panels) and side view (lower panels) of the optimized structures of three most stable adsorption states of  $\text{H}_2\text{O}/\text{Be}(0001)$  surface, i.e., top- $x$ , top- $y1$  and top- $y2$ , respectively. Gray, red and white balls denote Be, O, and H atoms, respectively.

high symmetry adsorption sites on Be(0001) surface is considered. The O atom of water is initially placed on the precise high-symmetry sites with various orientations of water with respect to the substrate. We find that there exist locally stable adsorption states on the top site of Be(0001), where the  $\text{H}_2\text{O}$  molecules lie fairly flat on the surface, labeled by employing the notations top- $x$ ,  $y1$  and  $y2$ , respectively. The structural and energetic details of the molecular states are illustrated and summarized in Figs. 1(b)-(d) and Table I, respectively. In Fig. 1(b) we define two angles  $\phi$  and  $\theta$ .  $\phi$  represents the azimuthal angle of  $\text{H}_2\text{O}$  with respect to the surface, and  $\theta$  represents the tilt angle between the  $\text{H}_2\text{O}$  molecular dipole plane and the surface. The adsorption energy of the system is calculated as follows:

$$E_{\text{ad}} = E_{\text{H}_2\text{O}/\text{Be}(0001)} - E_{\text{H}_2\text{O}} - E_{\text{Be}(0001)}, \quad (1)$$

where  $E_{\text{H}_2\text{O}}$ ,  $E_{\text{Be}(0001)}$ , and  $E_{\text{H}_2\text{O}/\text{Be}(0001)}$  are the total energies of the  $\text{H}_2\text{O}$  molecule, the clean Be surface, and the adsorption system respectively. According to this definition, a negative value of  $E_{\text{ad}}$  indicates that the adsorption is exothermic (stable) with respect to a free  $\text{H}_2\text{O}$  molecule and a positive value indicates endothermic (unstable) reaction.

From Table I, we can clearly see that at these stable adsorption sites, the work function 3.75 eV is much smaller than the clean Be(0001) surface (5.41 eV), implying an observable charge redistribution between the adsorbate water and the surface Be atoms. Take the

TABLE I: Calculated structural parameters, adsorption energy for a water molecule on Be(0001) surface.  $E_a$  (eV) represents the adsorption energy.  $\Phi$  (eV) represents the work function.  $z_O$  (Å) represents the vertical height of the O atom from the surface.  $d_{O-H}$  (Å) represents the bond length between the O and H atoms.  $\theta$  ( $^\circ$ ) represents the tilt angle between the  $H_2O$  molecular dipole plane and the surface.  $\alpha_{H-O-H}$  ( $^\circ$ ) represents the H-O-H bond angle.

Site	$E_a$	$\Phi$	$z_O$	$d_{O-H}$	$\theta$	$\alpha_{H-O-H}$
top- $x$	-0.300	3.75	1.79	0.98	21.6	106.3
top- $y1$	-0.303	3.75	1.79	0.98	20.7	106.4
top- $y2$	-0.300	3.75	1.79	0.98	20.6	106.4

adsorption site top- $y1$  for example, the O-H bond length 0.98 Å is almost identical to 0.97 Å of free  $H_2O$  molecule, but the H-O-H bond angle  $106.4^\circ$  is larger than that of free  $H_2O$ . The tilt angle is  $20.7^\circ$ , which is in line with the value of about  $20^\circ$  of the  $H_2O/Al(100)$  surface [12], but differing from that ( $\sim 10^\circ$ ) of the  $H_2O$ /transition metal surfaces, where the top site is also the most stable state. The adsorption energy  $-0.303$  eV indicates a weak molecule-surface interaction, and the molecular state may diffuse easily with a low barrier, passing through the bridge sites as a transition state, which will be discussed in the latter part of this paper. More interestingly, we find that for a  $H_2O$  molecule to reach the adsorption state, there does not exist any energy barrier, which means that  $H_2O$  can be adsorbed on the Be(0001) surface spontaneously. This is quite different from the adsorption of other molecules on the Be(0001) surface such as  $O_2$  [24] and CO [25], which need to overcome energy barriers.

As presented in Table I, the energetic differences among these three adsorption states on top site are very tiny. For further illustration, we investigate the azimuthal orientation of adsorbed  $H_2O$ , which is shown in Fig. 2. It can be seen that the favored orientation for  $H_2O$  at the top site is top- $y1$ . We can attribute this to the symmetry of the adsorption structure. The Be atom at the second layer (on the hcp site) of the substrate might also be partially responsible for this tiny azimuthal orientation preference. Nevertheless, it is apparent that the azimuthal rotation is facile, therefore the adsorption of  $H_2O$  on the top site is insensitive to the azimuthal orientation. In addition, a considerably less stable adsorption state, where

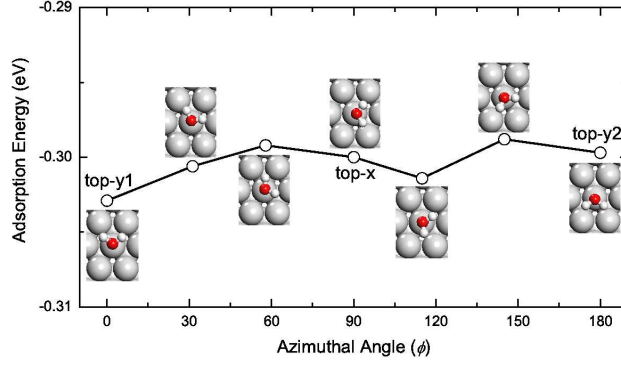


FIG. 2: (Color online) Calculated adsorption energy of H<sub>2</sub>O as a function of the azimuthal angle at the top site. The insets show the structures adopted in the calculations.

the water molecule is adsorbed on the top site in an upright configuration with the O atom down, is found by our calculations. the adsorption energy of this state is about 0.19 eV, which is also insensitive to the azimuthal orientation. In the following discussion, we will focus our attention on the the most stable flat-lying adsorption sites on the top site.

In order to gain more insights into the precise nature of the chemisorbed molecular state, the electronic PDOS of the H<sub>2</sub>O molecule and the topmost Be layer are calculated. As a typical example, here we plot in Fig. 3 the PDOS for the most stable adsorption configuration of top-y1. For comparison, the PDOS of the free H<sub>2</sub>O molecule and clean Be(0001) surface are also shown in Fig. 3. Three-dimensional (3D) electron density difference  $\Delta\rho(\mathbf{r})$ , which is obtained by subtracting the electron densities of noninteracting component systems,  $\rho^{\text{Be}(0001)}(\mathbf{r}) + \rho^{\text{H}_2\text{O}}(\mathbf{r})$ , from the density  $\rho(\mathbf{r})$  of the H<sub>2</sub>O/Be(0001) surface, while retaining the atomic positions of the component systems at the same location as in H<sub>2</sub>O/Be(0001), is also shown in the inset of Fig. 3(b). MOs  $2a_1$  and  $1b_2$  of water (not shown here) are far below the Fermi energy and thus remain intact in water-metal interaction. Here we consider only three MOs of water below the Fermi energy, i.e.,  $1b_2$ ,  $3a_1$  and  $1b_1$ . One can clearly see from Fig. 3(a) that after adsorption, these three MOs shift down in energy 3.8 eV, 4.8 eV and 4.9 eV, respectively. Compared to free water molecule, the distortion of the adsorbed water, i.e., the effect of water geometry, is pretty small (see Table I). Hence, these shifts of energy can be attributed to the interactions with the substrate. In addition to energy, it is noticeable that the MOs of adsorbed water are broaden apparently for  $1b_1$  and  $3a_1$ , which are known to have an oxygen lone-pair character perpendicular to the molecular plane, and

a mixture of partial lone-pair character parallel to the molecular plane and partial O-H bonding character, respectively [1]. Furthermore, despite little change in the PDOS near the surface Fermi energy, the water adsorption introduces new peaks for both  $s$  and  $p_z$  states of the surface Be atom, aligning in energy with  $1b_1$  and  $3a_1$ . Especially for  $3a_1$ , more electronic states of the Be atom appear nearby, compared with  $1b_1$ . This is quite in accordance with our above-mentioned result that the tilt angle of  $\text{H}_2\text{O}$  on the Be(0001) surface is larger than that on the transition metal surfaces, where only the  $1b_1$  dominates the water-surface interaction by coupling with atomic  $d$  orbital of the surfaces. Moreover, it may also give a reason why there exists a less stable adsorption state in an upright configuration on the top site.

All these features indicate a covalent coupling between the adsorbed water and the substrate. This result is substantiated by the 3D electron density difference. We can see that there exists a large charge accumulation between the adsorbate and substrate. As depicted by the PDOS, however, no apparent charge transfer between water and surface Be atom can be observed. In addition, we find that at the second layer of the surface, there exists a small charge depletion right at the fcc site, which possibly confirms our earlier speculation that the state top- $y1$  is most stable at the top site.

Given a  $\text{H}_2\text{O}$  molecule at a stable adsorption site, it is interesting to see how it can diffuse across the Be(0001) surface. Here, therefore, we calculate the diffusion paths and energetic barriers of water on Be(0001) surface between neighboring adsorption sites along the top- $x$ , top- $y1$  and top- $y2$  channels respectively, which are schematically shown in the insets of Fig. 4. The adsorption energies as a function of the lateral displacement of O atom are shown in Fig. 4. We can see that the activation energies for  $\text{H}_2\text{O}$  diffusion along the three paths are 0.289, 0.291 and 0.286 eV, respectively. The transition state of diffusion is located on the bridge site, which is not a stable adsorption site. The similarity of the energy barriers between these paths implies that it does not have a strong preference for a particular direction in which to diffuse, consistent with our previous analysis illustrated in Fig. 2. By assuming the attempt frequency  $10^{13}$  of the adsorbate, the energy barrier corresponds to diffusion temperature of about 113 K, suggesting that the diffusion can occur under room temperature on the  $\text{H}_2\text{O}/\text{Be}(0001)$  surface.

Finally let us discuss the possibility of dissociation of  $\text{H}_2\text{O}$  on the Be(0001) surface. Experimentally, it was found that beryllium can be oxidated by the water vapor [26]. Basically,

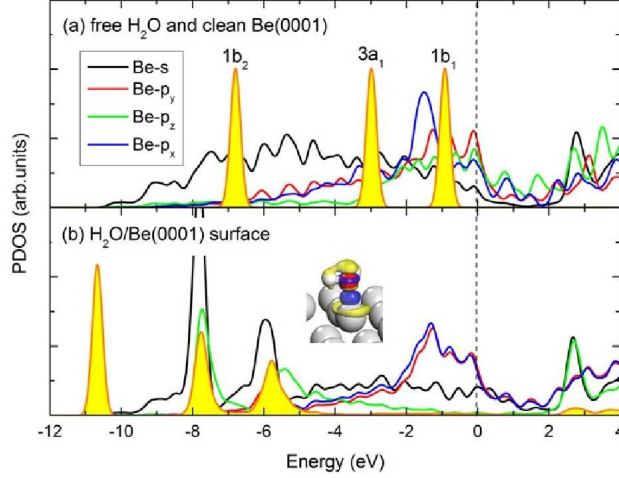


FIG. 3: (Color online) The PDOS for the H<sub>2</sub>O molecule and the top-layer Be atom bonded to H<sub>2</sub>O, at the stable adsorption site top- $\gamma_1$ : (a) free H<sub>2</sub>O and the clean Be(0001) surface, (b) the molecular state of H<sub>2</sub>O/Be(0001) surface, where the inset shows the 3D electron density difference, with the isosurface value set at  $\pm 0.025 e/\text{\AA}^3$ . The area filled with yellow color represents molecular orbital of H<sub>2</sub>O. The Fermi energy is set to zero.

since the binding strength of H<sub>2</sub>O/Be(0001) system is weak, hence one anticipates that it is not prone to dissociate for H<sub>2</sub>O on the ideal Be(0001) surface under low temperature. This is confirmed by our first-principles static as well as molecular dynamics simulations. We find that the hollow hcp and fcc sites are stable both for H and OH species on the Be(0001) surface. When we put the H and OH species simultaneously at two nearest-neighbor hollow sites, however, it turns out that they spontaneously combine together into H<sub>2</sub>O molecule finally without any barrier encountered. This is the same for the next-nearest-neighbor condition. The MD simulations are performed using the Verlet algorithm with a time step of 1 fs within the micro canonical ensemble. The O atom of the H<sub>2</sub>O molecule is initially set to be 4 Å away from the metal surface. The substrate atoms are initially at rest, while the initial kinetic energy of H<sub>2</sub>O is set to be 0.6 eV, with the initial velocity towards the substrate. In the same conditions it has been found that O<sub>2</sub> molecule would dissociate finally [27]. Here for H<sub>2</sub>O, nevertheless, it rapidly reaches a stable state that is similar to the adsorption state found above. Consequently, it proves that no dissociation state exists for the H<sub>2</sub>O/Be(0001) surface under room temperature. We speculate that the experimentally observed surface oxidation of beryllium by water vapor is closely related to the surface roughness or defects.



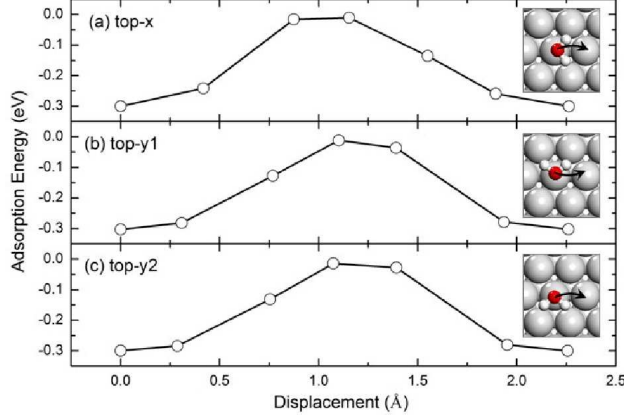


FIG. 4: Diffusion of  $\text{H}_2\text{O}$  on the top site of  $\text{Be}(0001)$  surface as a function of the lateral displacement of O atom from its original site top- $x$  (upper panel), top- $y1$  (middle panel), and top- $y2$  (lower panel), respectively.

In conclusion, we have systematically studied the adsorption behavior of  $\text{H}_2\text{O}$  on the  $\text{Be}(0001)$  surface by using first-principles DFT method. It has been found that the water molecule prefers to adsorb on the top site by lying fairly flat on the surface, insensitive to the azimuthal orientation and with a weak binding strength. It has been shown that the MO  $3a_1$ , as well as  $1b_1$ , plays an important role in  $\text{H}_2\text{O}$ -Be interaction by overlapping with the  $s$  and  $p_z$  states of the underlying beryllium atom. The diffusion energetics of  $\text{H}_2\text{O}$  on the top site across the  $\text{Be}(0001)$  surface has been calculated to display an energy barrier of about 0.3 eV. Moreover, no dissociation states of water molecule are found for the ideal  $\text{Be}(0001)$  surface.

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